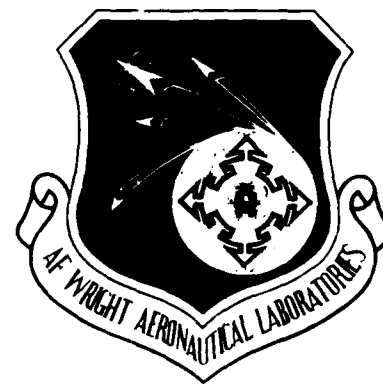


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HIGH ENERGY DENSITY SOLID AND LIQUID HYDROCARBON FUELS

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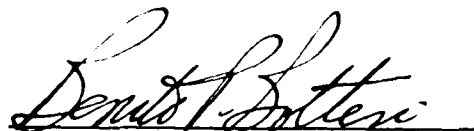


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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Oligomers of strained polycyclic cage monomers have been synthesized in an effort to prepare new candidate solid and liquid high energy/high density fuels for airbreathing missiles. Titanium-promoted dimerization of pentacyclo [5.4.0.0 <sup>2,6</sup> .0 <sup>3,10</sup> .0 <sup>5,9</sup> ] undecan-8-one affords a mixture of dimeric alkenes. Electrophilic addition of trifluoroacetic acid to the mixture of dimers thereby obtained has been studied. In the course of this work, new cage tri-fluoroacetates, alcohols, ketones, and hydrocarbons have been produced. Some structures have been determined by single crystal X-ray structural analysis. In addition, titanium-promoted dimerization of D-trishomocubanone has been utilized to synthesize a meso and a d,l dimeric alkene. All four of the hydrocarbon dimers are relatively nonvolatile, high-melting solids whose densities lie in the range 1.269-1.302 g-cm <sup>-3</sup> .					
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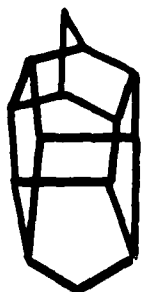
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## INTRODUCTION

The development of new high-energy hydrocarbon fuels for use in air-breathing missiles has been the objective of a number of investigations which have received support during the past decade through programs sponsored by the Air Force Systems Command<sup>1,2</sup> and/or the Naval Air Systems Command.<sup>3-5</sup> The key characteristics which must be met by potential cruise missile fuels have been described by Burdette and coworkers.<sup>6</sup> A primary requirement in this regard is that candidate fuels must possess high net volumetric heat of combustion (preferably greater than 160,000 BTU/gallon).<sup>2</sup> In order to meet the primary requirement of high net volumetric heat of combustion, hydrocarbon systems have been sought which maximize the ratio of carbon-atom to hydrogen-atom content; (i.e., hydrocarbons,  $C_nH_m$ , have been sought which maximize the ratio  $n/m$ . Bridged ring (polycyclic) hydrocarbon systems, by virtue of their high densities (concomitant with their compact structures), are particularly promising candidate fuels. Compounds of this type have already been utilized extensively as fuels for air-breathing missiles.

In the early stages of our study, one-pound samples of two particularly promising fuel candidates, 1 (heptacyclo[6.6.0.0<sup>2,6</sup>.0<sup>3,13</sup>.0<sup>4,11</sup>.0<sup>5,9</sup>.0<sup>10,14</sup>]tetradecane, HCTD) and 2 (pentacyclo[5.4.0.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>]undecane, PCUD, structures shown below) were synthesized.



1



2

Both compounds 1 and 2 display high densities (1.26 and 1.23 g-cm<sup>-3</sup>, respectively). The performance of each compound as a ramjet fuel has been evaluated by personnel at the Naval Weapons Center.<sup>7</sup> In addition, we have synthesized several derivatives of 1<sup>8</sup> and of 2<sup>9-11</sup>.

One difficulty attendant with the use of both HCTD and PCUD as fuels is their volatility. Although they are both high-melting solids, both hydrocarbons sublime readily and can escape from the binder (e.g., HTPB) on long standing at ambient temperature. In an effort to minimize the volatility of these systems (and thereby improve their combustion and storage characteristics) without sacrificing other desirable fuel properties, we have undertaken the synthesis of dimers and higher molecular weight oligomers that contain HCTD or PCUD units. In Figure 1, calculated heats of formation and densities of PCUD dimers are compared with the corresponding values for monomeric PCUD and for keto-derivatives of PCUD.

## RESULTS AND DISCUSSION

Our synthesis of PCUD dimers (via dimerization of PCUD-8-one with low-valent titanium)<sup>12</sup> is shown in Figure 2. Four possible dimers can result from this reaction; their respective structures and corresponding stereochemical designations are shown in FIGURE 3. Each of the four isomers possesses a twofold symmetry element (e.g., mirror plane, C<sub>2</sub> axis, or center of symmetry).

In our hands, titanium-promoted dimerization of PCUD-8-one (3) afforded a mixture of dimers, 4a-4d, as expected. A sample of the mixture of isomeric dimers thereby obtained (ca. 25 grams) was submitted to personnel at Wright-Patterson AFB for further study. Careful fractional recrystallization of this mixture from hexane afforded a single isomer, 4a, mp 214-215 °C. This

isomer was shown to possess the  $E_{syn}$  configuration via single crystal X-ray structural analysis (Figure 4; unit cell parameters are shown in Figure 5).<sup>13</sup> Particularly noteworthy is the unusually high crystal density of the  $E_{syn}$  PCUD dimer, i.e.,  $1.284 \text{ g-cm}^{-3}$  (calculated from the X-ray data).

More recently, the remaining three isomers (i.e., 4b-4d) have been isolated by a combination of column chromatographic techniques and fractional recrystallization (see Experimental Section). Ultimately, we hope to obtain X-ray data that will permit unequivocal assignment of the structure of each of the three remaining PCUD dimers.

We have also synthesized mixtures of monomethyl-PCUD dimers (Figure 6). In response to the need for high-density liquid fuels, we undertook this synthesis in the hope that the product, a gross mixture of many isomeric dimers, might be either a low-melting solid or a dense liquid. The procedure shown in Figure 6 afforded a sticky, semi-solid material which gradually solidified on standing to afford a material with mp 100-110 °C. A sample of the mixture of isomeric dimers thereby obtained (ca. 25 grams) was submitted to personnel at Wright-Patterson AFB for further study.

Recently, we have undertaken a study of electrophilic additions to our PCUD dimers (individually and in the gross mixture of four dimers that results via titanium-promoted dimerization of PCUD-8-one). This was done for several reasons: First, we were interested in determining whether structural differences among the various dimers would lead to differences in reactivity toward the electrophilic reagent, HX. If this is indeed the case, then it may be possible to separate one or possibly two of the dimers from the mixture by taking advantage of these differential reactivities. Secondly, we anticipated that Wagner-Meerwein rearrangements might occur in carbonium ion



intermediates, thereby leading to the formation of interesting new  $C_{22}$  compounds that are not easily accessed via direct, titanium-promoted dimerization reactions. Finally, we are interested in determining whether or not structural differences among the various PCUD dimers might affect the mode of addition (syn vs. anti) of HX across the C=C double bond of each dimer.

The anticipated course of electrophilic addition to PCUD dimers is illustrated for the addition of trifluoroacetic acid to 4a in Figure 7. The reaction sequence shown in this figure has been performed by using the mixture of four PCUD dimers as substrate. The results are shown in Figure 8. When the reaction with  $CF_3CO_2H$  was performed at room temperature in chloroform solvent, a mixture of two trifluoroacetate adducts (5a and 5b) was formed (60 percent) along with a mixture of two unreacted PCUD dimers (16.7 percent). The mixture of 5a and 5b was then subjected to hydrolysis with aqueous base, thereby affording a mixture of alcohols, 6a and 6b. The resulting mixture of alcohols was oxidized subsequently by using pyridinium chlorochromate (PCC) in methylene chloride solvent; the product was found to be a mixture of two isomeric ketones, 7a and 7b. This mixture of ketones was separated by flash column chromatography followed by fractional recrystallization. The structures of 7a and 7b each have been established unequivocally by single crystal X-ray structural analysis, (Figures 9 and 10, respectively).

Subsequently, we subjected the unreacted dimer (recovered from the above reaction; mixture of two isomers) with trifluoroacetic acid in refluxing chloroform. Addition of trifluoroacetic acid to the C=C double bond in the mixture of dimers occurred under these conditions. Basic hydrolysis of the trifluoroacetate adduct followed by oxidation with PCC again afforded a

mixture of two isomeric ketones (Figure 11). Efforts to characterize the individual ketones thereby obtained are underway at present.

Recently, we have studied the Wolff-Kishner reduction of isomerically pure ketones 7a and 7b. Of particular interest is the fact that the hydrocarbons thereby obtained differ substantially in melting point. The product of Wolff-Kishner reduction of 7a (i.e., 8a) displays mp 114-115 °C, whereas the corresponding product obtained by Wolff-Kishner reduction of 7b (i.e., 8b) displays mp 74-75 °C. We have obtained the X-ray structure of 8a (Figure 12); the crystal density of 8a was found to be 1.290 g-cm<sup>-3</sup>.

As an extension of the forgoing study, we have prepared dimers of D<sub>3</sub>-trishomocubane by titanium-promoted dimerization of the corresponding monomeric trishomocubanone (9). In this case, only two dimers [i.e., 10a (meso) and 10b (d,l)] can result from this reaction (Figure 13). A small sample (ca. 1 gram) of a mixture of 10a and 10b has been sent to personnel at Wright-Patterson AFB for further study. Careful fractional recrystallization of the mixture of dimers thereby obtained from ligroin afforded a single isomer, mp 246 °C. This dimer was shown to possess the meso configuration (i.e., 10a) by single crystal X-ray structural analysis (Figure 14).<sup>14</sup> Of particular significance is the unusually high density of this compound, i.e., 1.302 g-cm<sup>-3</sup>. Meso isomer 10a crystallizes in the C2/c space group (monoclinic).

More recently, we have isolated the corresponding d,l dimer, 10b, mp 186 °C, and we have obtained its structure by single crystal X-ray structural analysis (Figure 15). Interestingly, the density of 10b (1.269 g-cm<sup>-3</sup>) is significantly lower than that of its isomer, 10a. The d,l dimer, 10b, crystallizes in the P1 space group (triclinic).

Two important results of that have emerged from the studies described above are noteworthy. First, the calculated crystal densities of the  $E_{syn}$  PCUD dimer (4a), of the rearranged cage hydrocarbon 8a, and of 10a and 10b (i.e., 1.284, 1.290, 1.302, and 1.269 g-cm<sup>-3</sup>, respectively) rank among the highest known hydrocarbon densities; [compare these values with the densities of cubane (1.29 g-cm<sup>-3</sup>),<sup>15</sup> 1,16-dimethyldodecahedrane (1.412 g-cm<sup>-3</sup>)<sup>16</sup> and dodecahedrane (1.448 g-cm<sup>-3</sup>)<sup>17</sup>]. Cubane has been made in gram quantities, whereas dodecahedranes have been made only in milligram quantities. In contrast, we have the capability to synthesize routinely multi-gram (or even kilogram) quantities of PCUD and HCTD cage dimers!

Second, it is important to note that all of the three dimeric alkenes, i.e., 4a, 10a, and 10b, whose X-ray crystal structures have been determined thus far in our study, are all C<sub>22</sub>H<sub>24</sub> isomers that possess distinctly different crystal densities. Any of the existing calculational methods that are used to estimate crystal densities are based upon molecular formula and functional group additivity and therefore are incapable of predicting variations in densities among geometric isomers.<sup>18</sup> Hence, all of our C<sub>22</sub>H<sub>24</sub> isomers are predicted by any of these methods to possess the same density. In particular, we note that whereas the  $E_{syn}$  and  $Z_{syn}$  isomers (i.e., 4a and 4b, respectively) are "C-shaped," the corresponding  $E_{anti}$  and  $Z_{anti}$  isomers (i.e., 4c and 4d, respectively) are "S-shaped." It seems illogical to suppose that isomers which possess such radically different overall molecular configurations should nevertheless display identical molar volumes and, hence, should possess identical densities! This point is emphasized further by the dramatic difference between the crystal densities of isomeric dimers 10a and 10b (i.e., 1.302 and 1.269 g-cm<sup>-3</sup>, respectively)! There is, in fact, a limited amount of

published experimental evidence that is relevant to this point: Paquette and coworkers<sup>19</sup> have reported the crystal densities of a series of isomeric dinitro-1,3-bishomopentaprismanes that differ from one another only in the relative configurations of their two C-NO<sub>2</sub> bonds. Significant variations in crystal densities were observed among the compounds studied.

One of our interests is to determine the crystal densities of as many of the individual C<sub>22</sub>H<sub>24</sub> isomers as possible and to utilize this data to develop a molecular geometry-based approach for predicting crystal densities.<sup>18</sup> In addition, we are interested in determining configurational and conformational effects upon proton and carbon-13 NMR chemical shifts and coupling constants in rigid cage systems.<sup>20</sup>

#### SUMMARY AND CONCLUSIONS

Our efforts to synthesize oligomers of strained polycyclic cage monomers have resulted in the synthesis of novel cage dimers 4a-4d, 10a and 10b, along with derivatives of these systems. These dimers possess unusually high crystal densities and are relatively nonvolatile; both properties are considered to be desirable for new candidate fuel systems. The electrophilic addition of trifluoroacetic acid to a mixture of PCUD dimers, 4a-4d, has been studied, and several reaction products have been characterized by single crystal X-ray structural analysis. Future studies will be directed toward: (i) the synthesis of oligomers of HCTD (1) and (ii) studies of reactions of 10a and 10b with a variety of electrophiles.

#### EXPERIMENTAL SECTION

Melting points are uncorrected.

**Titanium-promoted Dimerization of 3.** A solution of TiCl<sub>4</sub> (28.4 g, 150 mmol) in anhydrous tetrahydrofuran (THF, 500 mL) was cooled to 0 °C by

application of an external ice bath. To the stirred, cooled suspension was added zinc dust (20 g, 0.3 g-atom) under an argon atmosphere in small portions during 1 h. The temperature of the reaction mixture was maintained between 0 °C and 10 °C during this time. After all of the zinc dust had been added, dry pyridine (10 mL) was added, the cold bath was removed, and the reaction mixture was allowed to warm to room temperature. The reaction mixture was stirred at room temperature for 0.5 h and then refluxed for an additional 20 minutes. The resulting black mixture was then cooled to 0 °C, and a solution of pentacyclo[5.4.0.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>]-undecan-8-one (3, 22.4 g, 140 mmol) in anhydrous THF (50 mL) was added dropwise under argon during 15 minutes. The resulting mixture was stirred at 0-5 °C for 1 h. The reaction mixture was then refluxed under argon for 3 days, at which time the resulting mixture was cooled to 0 °C and quenched by slow addition of 10 percent aqueous potassium carbonate solution (300 mL). The reaction mixture was concentrated in vacuo; THF (ca. 400 mL) was removed from the reaction mixture in this manner. The resulting mixture was extracted with ether (4 x 75 mL). The combined organic layers were washed successively with 10 percent aqueous hydrochloric acid (3 x 50 mL), water (3 x 50 mL), and brine (2 x 50 mL), dried (anhydrous sodium sulfate), and filtered. The filtrate was concentrated in vacuo; the sticky semisolid residue thereby obtained, upon trituration with methanol, afforded a mixture of four alkene dimers (4a-4d, 9.5 g, 50 percent) as a colorless microcrystalline solid, mp 176-190 °C. Concentration of the methanolic mother liquor in vacuo afforded pentacyclo[5.4.0.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>]-undecan-8-ol (5 g, 20 percent), mp 228-229 °C. The recovered cage alcohol was oxidized to 3 and recycled.

The crude mixture of dimers 4a-4d was purified by flash column chromatography (silica gel stationary phase, ethyl acetate eluent). Two fractions, each of which contained two isomeric dimers (as judged by examination of their respective carbon-13 NMR spectra), were thereby obtained. Each of the dimers was then re-chromatographed through a long flash chromatography column (silica gel stationary phase, hexane eluent). In this manner, separation of the crude mixture of dimers into its four pure components was carried out. Spectral properties of each dimer are given below:

**Dimer 4a** (mp 214-215 °C): IR (KBr) 2915 (vs), 2842 (s), 1435 (m), 1280 (m), 1250  $\text{cm}^{-1}$  (m);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.15 (m, 1 H), 1.25 (m, 1 H), 1.62 (m, 2 H), 2.22 (m, 2 H), 2.33 (m, 1 H), 2.58 (m, 2 H), 2.75 (m, 2 H), 3.12 (m, 1 H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  31.08 (t), 35.40 (t), 39.30 (d), 39.92 (d), 43.07 (d), 43.37 (d), 45.54 (d), 46.54 (d), 46.80 (d), 47.54 (d), 133.40 (s); mass spectrum (70 eV),  $m/e$  (relative intensity) 290 (2.1) 289 (11.7), 288 (molecular ion, 56.5), 222 (100.0), 209 (48.4), 156 (83.3), 141 (59.0), 115 (71.2), 79 (84.0), 39 (30.6). The structure of 4a was established via single crystal X-ray structural analysis (see Figure 4).

Anal. Calcd for  $\text{C}_{22}\text{H}_{24}$ : C, 91.67; H, 8.33. Found: C, 91.49; H, 8.53.

**Dimer 4b** (mp 201-201.5 °C):  $^{13}\text{C}$  NMR ( $\text{CCl}_4$ )  $\delta$  30.39 (t), 34.87 (t), 38.51 (d), 39.10 (d), 42.34 (d), 42.65 (d), 44.76 (d), 45.69 (d), 45.97 (d), 46.83 (d), 132.57 (s).

Anal. Calcd for  $\text{C}_{22}\text{H}_{24}$ : C, 91.67; H, 8.33. Found: C, 91.61; H, 8.08.

**Dimer 4c** (mp 204.0-204.5 °C):  $^{13}\text{C}$  NMR ( $\text{CCl}_4$ )  $\delta$  30.51 (t), 34.98 (t), 38.65 (d), 39.25 (d), 42.47 (d), 42.60 (d), 44.85 (d), 45.91 (d), 46.08 (d), 47.02 (d), 132.45 (d).

Anal. Calcd for  $C_{22}H_{24}$ : C, 91.67; H, 8.33. Found: C, 91.84; H, 8.04.

Dimer 4d (mp 217-218 °C):  $^{13}C$  NMR ( $CCl_4$ )  $\delta$  30.93 (t), 35.27 (t), 39.18 (d), 39.81 (d), 42.96 (d), 43.25 (d), 45.43 (d), 46.44 (d), 46.69 (d), 47.43 (d), 133.45 (s).

**Acid Catalyzed Rearrangement of 4a.** To a solution of 4a (1.8 g., 6.2 mmol) in chloroform (50 mL) was added trifluoroacetic acid (2.00 g, 17.5 mol). The resulting solution immediately turned pink; after stirring at room temperature for 0.5 h, the color had darkened to purple. After stirring at room temperature for an additional 4 h, the reaction was quenched by addition of solid sodium bicarbonate (2.0 g, 24 mmol). The resulting mixture was extracted successively with 10 percent aqueous sodium bicarbonate solution (3 x 20 mL), water (3 x 30 mL), and brine (30 mL), dried (anhydrous sodium sulfate), and filtered. The filtrate was concentrated in vacuo, and the residue was purified by column chromatography (silica gel stationary phase, hexane eluant). A mixture of two isomeric products (5a and 5b, 1.5 g 60 percent) was thereby obtained along with unreacted 2 (isolated as a mixture of two of the four isomers, 2a-2d, 300 mg. 16.7 percent). IR of the mixture of 5a and 5b (neat): 2930 (s), 2840 (m), 1760  $cm^{-1}$ (s). This mixture of 5a and 5b was used as obtained without further purification or characterization.

**Hydrolysis of the Mixture of 5a and 5b.** To a solution of the mixture of 5a and 5b (1.4 g, 3.5 mmol) in THF (40 mL) was added 10 percent aqueous sodium hydroxide solution (10 mL). The reaction mixture was stirred at room temperature for 1 h. The resulting alkaline solution was cooled to 10 °C by application of an external ice bath, and the pH of this solution was adjusted to pH 4.0 by dropwise addition of 10 percent aqueous hydrochloric acid solution (20 mL). The resulting solution was then extracted with ether (3 x

25 mL). The combined organic extracts were washed successively with water (2 x 20 mL) and with brine (2 x 30 mL), dried (anhydrous sodium sulfate), and filtered. The filtrate was concentrated in vacuo to afford a mixture of alcohols 6a and 6b (1.0 g, 93.4 percent) as a colorless oil: IR (neat) 3500-3100 (s), 2840  $\text{cm}^{-1}$  (m). This mixture of 6a and 6b was used as obtained without further purification or characterization.

**Oxidation of the Mixture of 6a and 6b.** To a solution of the mixture of 6a and 6b (900 mg, 2.94 mmol) in methylene chloride (20 mL) was added pyridinium chlorochromate (PCC, 3.00 g, 13.9 mmol), and the resulting mixture was stirred at room temperature for 1.5 h. The reaction mixture then was poured into ether (100 mL), and the resulting mixture was filtered through Celite. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (silica gel stationary phase, 1 percent ethyl acetate-hexane mixed solvent as eluent). Two isomeric ketones, 7a (0.34 g, 38 percent) and 7b (0.31 g, 34.8 percent), were thereby obtained.

Recrystallization of 7a from methanol-ethyl acetate mixed solvent afforded analytically pure material: mp 105.0-105.5 °C; IR (KBr) 2930 (s), 2840 (s), 1740  $\text{cm}^{-1}$  (s);  $^{13}\text{C}$  NMR  $1(\text{CDCl}_3)$   $\delta$  26.73 (t), 33.30 (t), 33.95 (t), 35.77 (t), 36.16 (d), 36.55 (d), 38.96 (d), 40.32 (d), 42.27 (d), 42.53 (d), 42.73 (d), 43.64 (d), 43.90 (d), 45.59 (d), 45.98 (d), 46.76 (d), 47.28 (d), 47.47 (d), 47.60 (d), 50.92 (d), 55.93 (s), 216.,88 (s). The structure of 7a was established unequivocally via single crystal X-ray structural analysis (see Figure 9).

Anal. Calcd for  $\text{C}_{22}\text{H}_{24}\text{O}$ : C, 86.84; H, 7.89. Found: C, 86.85; H, 8.01.

Recrystallization of 7b from hexane afforded analytically pure material: mp 106.5-107.0 °C; IR (KBr) 2930 (s), 2840 (s), 1740  $\text{cm}^{-1}$  (s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )



$\delta$  26.80 (t), 33.43 (t), 34.34 (t), 35.71 (t), 36.36 (d), 37.01 (d), 39.61 (d), 40.71 (d), 40.77 (d), 40.92 (d), 42.73 (d), 42.92 (d), 44.03 (d), 44.42 (d), 44.68 (d), 45.20 (d), 46.24 (d), 47.28 (d), 47.67 (d), 49.69 (d), 56.78 (s), 218.05 (s). The structure of 7b was established unequivocally via single crystal X-ray structural analysis (see Figure 10).

Anal. Calcd for  $C_{22}H_{24}O$ : C, 86.84; H, 7.89. Found: C, 86.72; H, 7.94.

**Wolff-Kishner Reduction of 7a.** A mixture of 7a (100 mg, 0.33 mmol), potassium hydroxide (450 mg, 7.9 mmol), anhydrous hydrazine (8.98 g, 280 mmol), diethylene glycol (5 mL), and water (2 mL) was heated with stirring at ca. 110 °C for 3 h. The reaction vessel was fitted with a Dean-Stark apparatus, and a mixture of water and hydrazine (ca. 10 mL) was removed by azeotropic distillation. During this operation, the temperature of the reaction mixture rose to 210 °C. The resulting mixture was heated with stirring at 200-210 °C for 3.5 h. The reaction mixture was then allowed to cool gradually to room temperature, and water (15 mL) was added. The pH of the resulting mixture was adjusted to pH 4.0 by dropwise addition of concentrated aqueous hydrochloric acid (ca. 4 mL). The mixture was then extracted with hexane (3 x 30 mL). The combined organic extracts were washed successively with water (3 x 30 mL) and with brine (2 x 30 mL), dried (anhydrous sodium sulfate), and filtered. The filtrate was concentrated in vacuo, thereby affording 8a (85 mg, 89 percent). Fractional recrystallization from hexane afforded pure 8a as a colorless microcrystalline solid: mp 117 °C; IR (KBr) 2920 (s), 2840 (m), 1440 (M), 1240  $cm^{-1}$  (s);  $^{13}C$  NMR ( $C_6D_6$ )  $\delta$  26.98 (t), 31.27 (t), 33.60 (t), 33.75 (t), 36.10 (d), 36.82 (t), 38.32 (d), 38.99 (d), 42.84 (d), 42.94 (d), 43.27 (d), 43.60 (d), 44.19 (d), 45.57 (d), 46.29 (d), 46.52 (d), 47.26 (d), 47.32 (d), 47.46 (d), 47.58 (d), 47.91 (d),

58.16 (s); mass spectrum (70 eV),  $m/e$  (relative intensity) 290 (molecular ion, 36.0), 224 (100 percent). The structure of 8a was established unequivocally via single crystal X-ray structural analysis (see Figure 11).

Anal. Calcd for  $C_{22}H_{24}$ : C, 90.97; H, 9.02. Found: C, 90.96; H, 9.15.

**Wolff-Kishner Reduction of 7b.** Reduction of the carbonyl group in 7b was performed by using the same procedure as that described above for the corresponding reduction of 7a. Hydrocarbon 8b (86 mg, 90 percent) was thereby obtained. Fractional recrystallization from hexane afforded pure 8b as a colorless microcrystalline solid: mp 78-79 °C; IR (KBr) 2930 (s), 2860 (m), 1440 (m), 1250  $cm^{-1}$  (m);  $^{13}C$  NMR ( $C_6D_6$ )  $\delta$  27.33 (t), 31.89 (t), 33.97 (t), 34.36 (t), 36.70 (d), 37.67 (t), 39.23 (d), 39.36 (d), 43.14 (d), 43.39 (d), 43.66 (d), 44.44 (d), 44.63 (d), 44.83 (d), 45.99 (d), 46.65 (d), 46.91 (d), 47.95 (d), 48.14 (d), 49.25 (d), 50.94 (d), 58.94 (s); mass spectrum (70 eV),  $m/e$  (relative intensity) 290 (molecular ion, 35.0), 224 (100 percent).

Anal. Calcd for  $C_{22}H_{24}$ : C, 90.97; H, 9.02. Found: C, 90.96; H, 9.13.

**Titanium-promoted Dimerization of  $D_3$ -Trishomocubanone (9).** To a 100 mL three-neck round bottom flask was added dry THF (30 mL) under an argon atmosphere. The THF was cooled via application of an external ice bath. To the cooled, stirred solvent was added titanium tetrachloride (2.02 g, 10.5 mmol) via syringe. To the resulting turbid yellow mixture was added powdered zinc (1.43 g, 21.8 mmol) portionwise with stirring. After all of the zinc had been added, the cold bath was removed, and the mixture was heated and refluxed for 1 h. The mixture was then allowed to cool gradually to room temperature, whereupon pyridine (0.5 mL) was added followed by a solution of  $D_3$ -trishomocubanone (7, 1.6 g, 10 mmol) in dry THF (10 mL). The resulting mixture was refluxed under argon for 24 h. The reaction mixture was then

allowed to cool slowly to ambient temperature. The reaction mixture was further cooled via application of an external ice bath, and the cooled solution was quenched via gradual addition of 10 percent aqueous potassium carbonate solution (ca. 50 mL, excess). The reaction mixture was transferred into a 500 mL conical flask that contained diethyl ether (200 mL). The resulting mixture was stirred vigorously for 10 minutes and then filtered. The residue was washed thoroughly with ether (2 x 100 mL) and then discarded. The layers in the filtrate were then separated, and the aqueous layer was extracted with ether (2 x 100 mL). The combined ether layers were washed sequentially with water (200 mL), 5 percent aqueous hydrochloric acid solution (2 x 100 mL), water (2 x 200 mL), and brine (100 mL). The organic layer was dried (anhydrous sodium sulfate) and filtered, and the filtrate was concentrated in vacuo. The residue was purified via careful column chromatography (silica gel stationary phase). Elution with hexane afforded a mixture of meso- and d,l-trishomocubane dimers (10a and 10b, respectively, 864 mg, 60 percent). Further elution of the chromatography column with chloroform afforded pentacyclo[6.3.0.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>]undecan-4-ol (405 mg, 25 percent), mp 166-168 °C (lit<sup>21</sup> mp 167-168 °C).

The mixture of dimers 10a and 10b was separated by flash column chromatography (silica gel stationary phase, hexane eluent). Under these conditions, the d,l dimer, 10b, eluted first from the column, followed shortly thereafter by meso dimer, 10a. Individual isomers were further purified by fractional recrystallization from hexane. Spectral properties of each isomer are given below:

Dimer 10a (mp 246 °C): IR (KBr) 3006 (s), 2978 (s), 2908 (s), 1465 (w), 1302 (w), 1288 (m), 1276 (w), 1107 (w), 1048 (w), 1034 (w), 980 (w), 794 cm<sup>-1</sup>

(w);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.40 (m, 8H), 1.95-2.08 (m, 8H), 2.15-2.24 (m, 4 H), 2.35-2.45 (m, 4 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  34.24 (t), 42.96 (d), 47.73 (d), 47.75 (d), 49.40 (d), 131.28 (s); mass spectrum (70 eV), m/e (relative intensity) 288 (molecular ion, 36.2), 222 (100.0).

Anal. Calcd for  $\text{C}_{22}\text{H}_{24}$ : C, 91.61; H, 8.39. Found: C, 91.52; H, 8.41.

Dimer 10b (mp 186 °C): IR (KBr) 2988 (s), 2910 (s), 1466 (w), 1293 (m), 1277 (m), 1050 (w), 978 (w),  $795\text{ cm}^{-1}$  (m);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.40 (m, 8 H), 1.9-2.5 (m, 16 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  34.26 (t), 42.90 (d), 47.71 (d), 47.85 (d), 49.40 (d), 131.22 (s); mass spectrum (70 eV), m/e (relative intensity) 288 (molecular ion, 33.9), 222 (100.0).

Anal. Calcd for  $\text{C}_{22}\text{H}_{24}$ : C, 91.61; H, 8.39. Found: C, 91.73; H, 8.43.

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COMPOUND	FORMULA	Calculated Values*	
		$\Delta H_f^\circ$ (kcal/mol)	$\rho$ (g-cm <sup>-3</sup> )
	$C_{11}H_{10}O_2$	-24.40	1.44 1.38 (observed)
	$C_{11}H_{12}O$	+1.51	1.34
	$C_{11}H_{14}$	+27.42	1.23
 (Dimer)	$C_{22}H_{24}$	+97.54	1.29
 (Saturated Dimer)	$C_{22}H_{26}$	+67.76	1.26

#### \*References

Method utilized for calculation of  $\Delta H_f^\circ$  values: Report on "Study of Pure Explosive Compounds. Part II, Correlation of Thermal Quantities with Explosive Properties", Office of the Chief of Ordnance Contract Number W-19-020-ORD-6436, Report No. C-57625, April 2, 1947.

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Figure 1. Calculated heats of formation and densities of PCUD and related systems

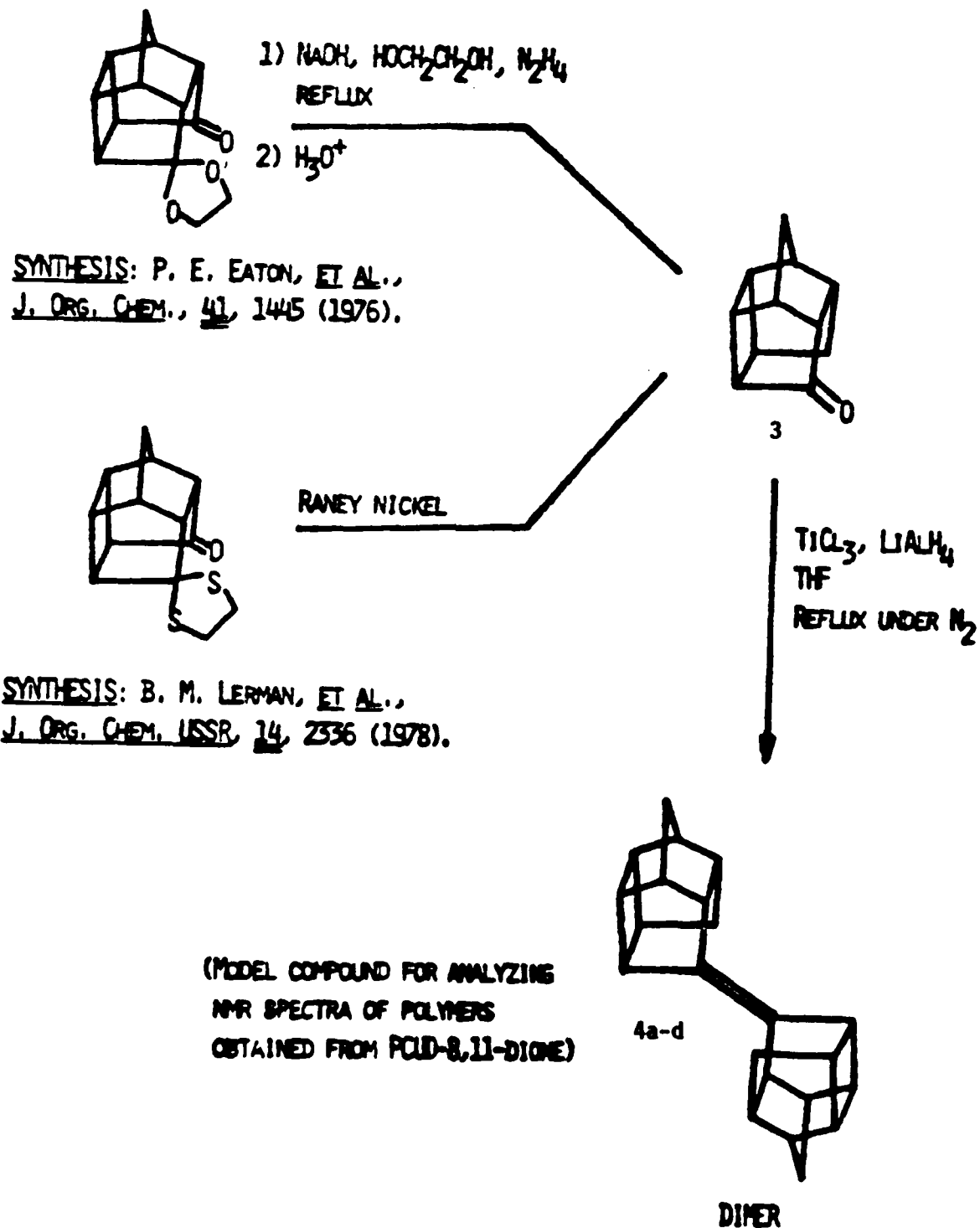


Figure 2. Synthesis of PCUD Dimers



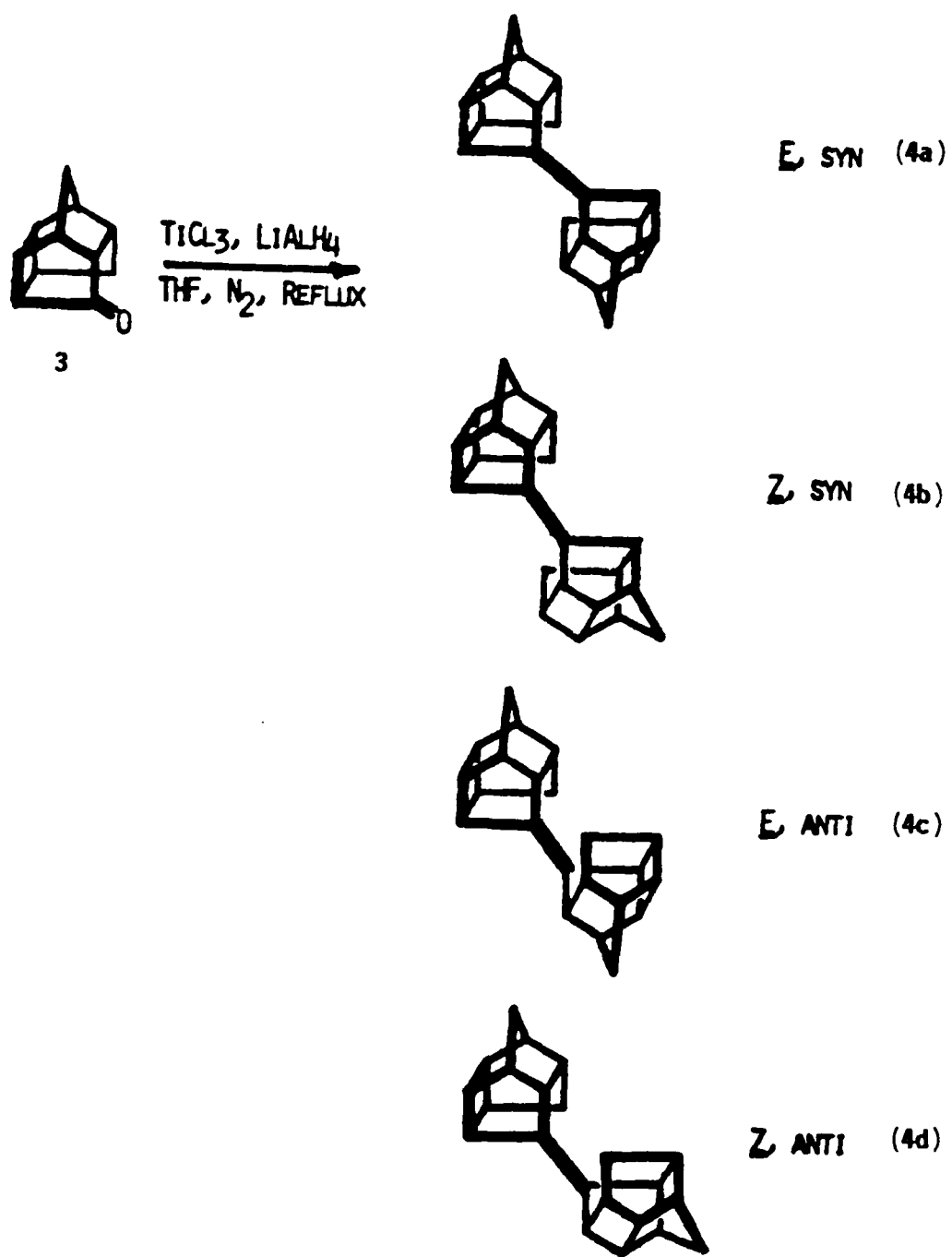


Figure 3. Structures of the Four Possible PCUD Dimers, 4a-4d

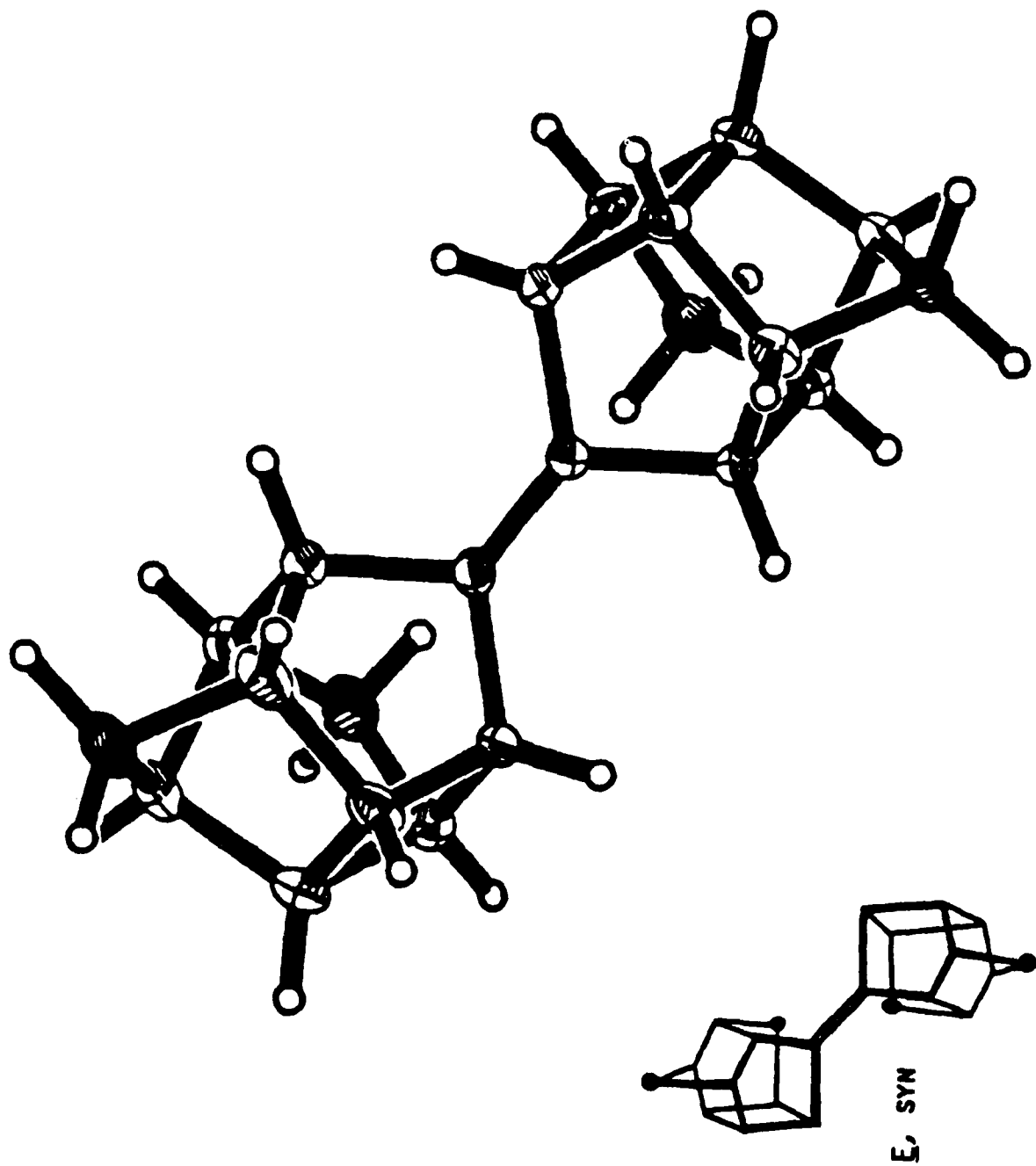
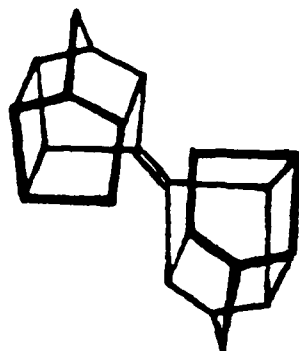


Figure 4. Structure drawing of 4a



**E,SYN DIMER (4a)**

**RESULTS OF SINGLE CRYSTAL X-RAY ANALYSIS**

$$A = 6.613(1) \text{ \AA}$$

$$B = 10.809(2) \text{ \AA}$$

$$C = 10.993(2) \text{ \AA}$$

$$\alpha = 97.5(2)^\circ$$

$$\beta = 9.8(1)^\circ$$

$$\gamma = 99.3(2)^\circ$$

**SPACE GROUP  $P_1$**

**TRICLINIC**

**DENSITY (CALCD)  $1.284 \text{ g-cm}^{-3}$**

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RICHARD GILARDI  
CLIFFORD GEORGE**

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Figure 5. Unit Cell Parameters for 4a

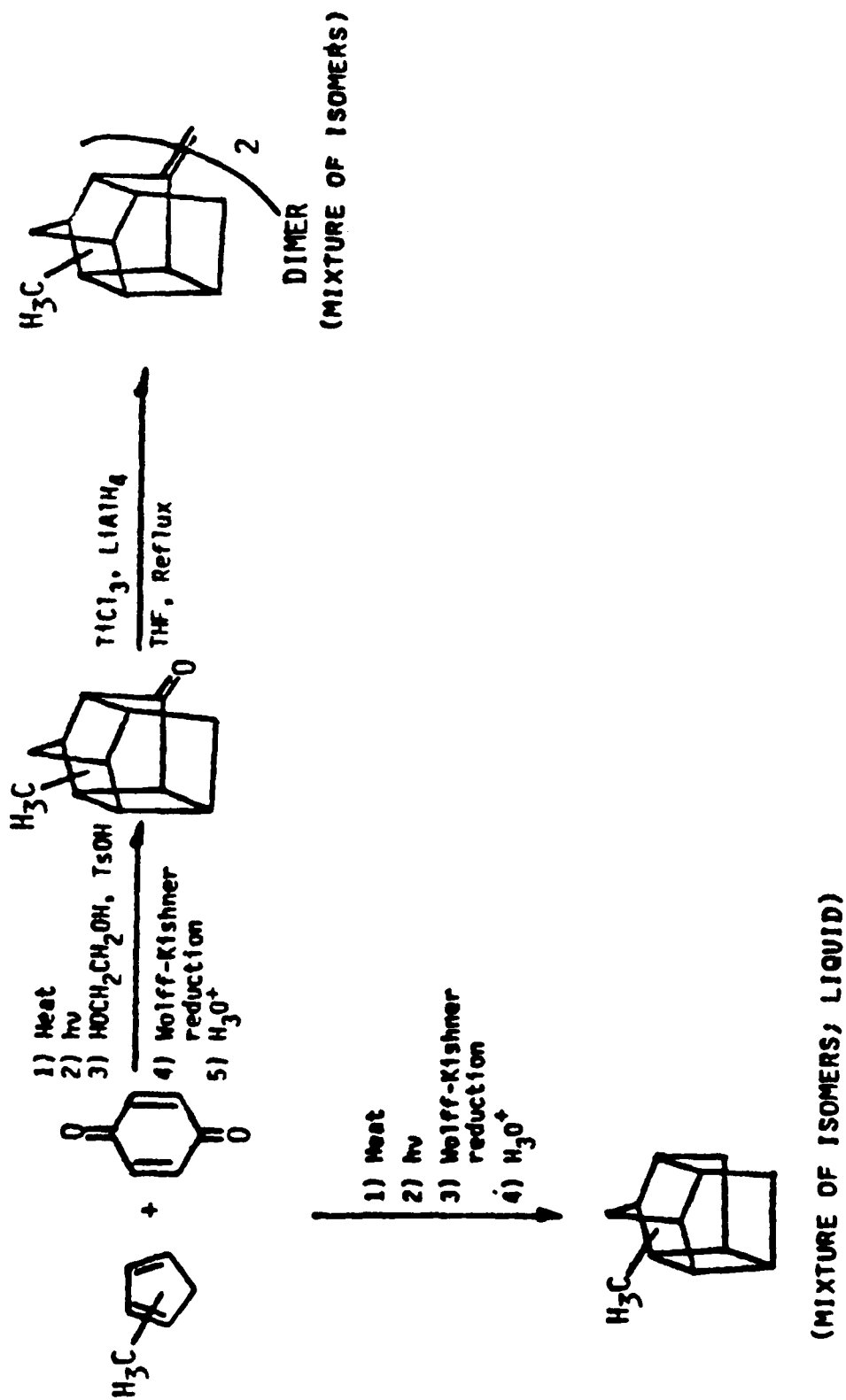
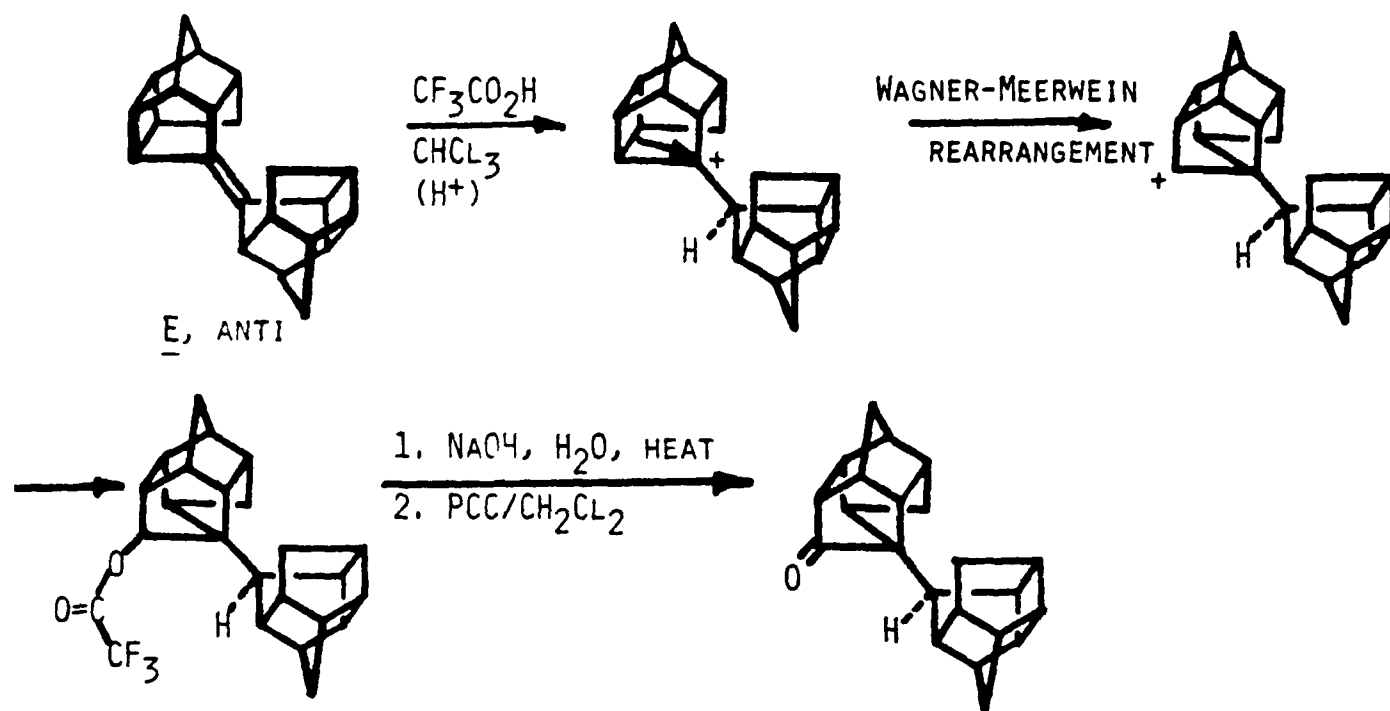


Figure 6. Synthesis of monomethylated PCUD dimers

# ELECTROPHILIC ADDITIONS OF $\text{CF}_3\text{CO}_2\text{H}$ TO THE $\text{C}=\text{C}$ DOUBLE BOND IN PCUD DIMERS



THE OTHER PCUD DIMERS (I.E., *Z*,ANTI, *Z*,SYN AND *E*,SYN) CAN REACT IN ANALOGOUS FASHION.

Figure 7. Anticipated course of electrophilic addition of trifluoroacetic acid to PCUD dimers 4a-d

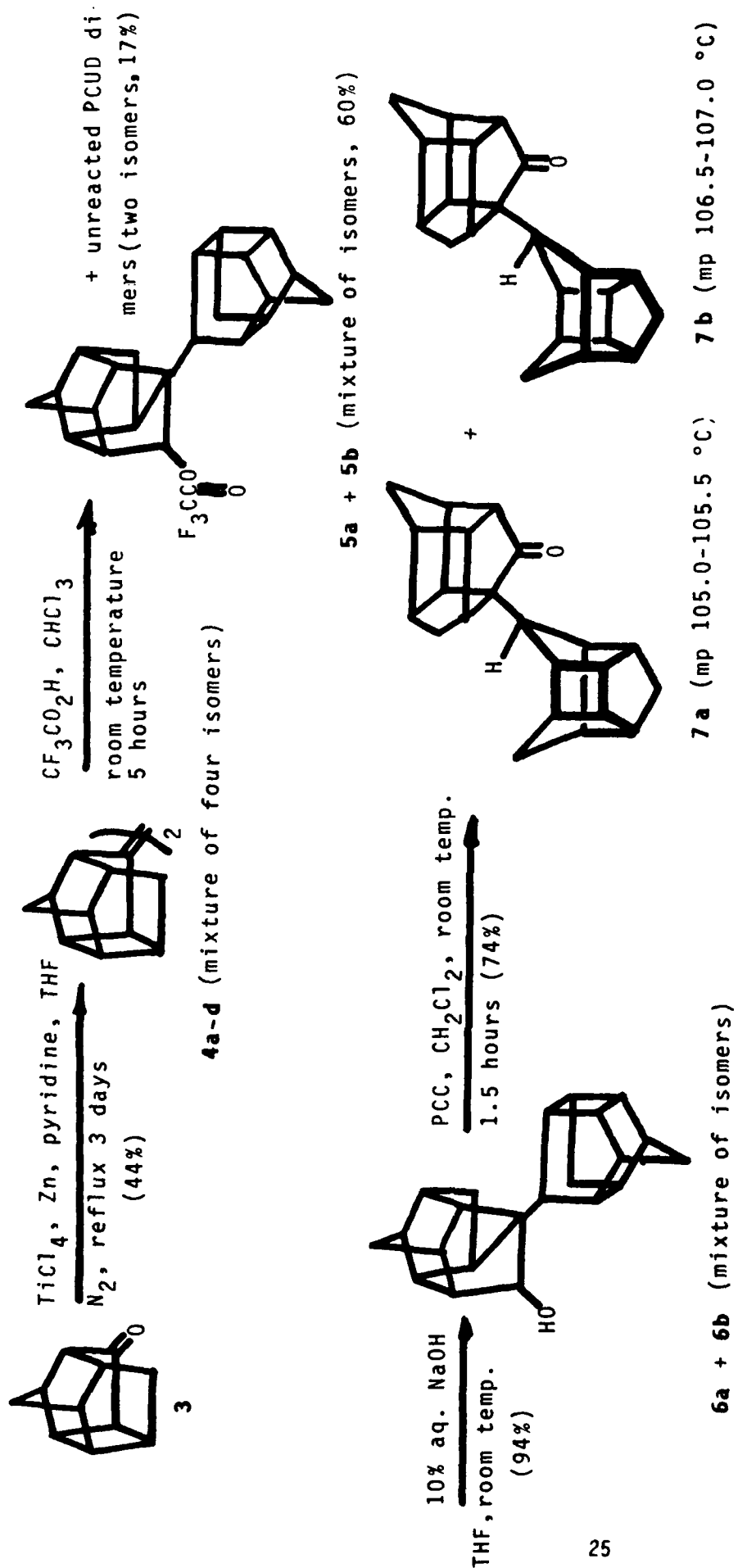


Figure 8. Synthesis of **7a** and **7b**

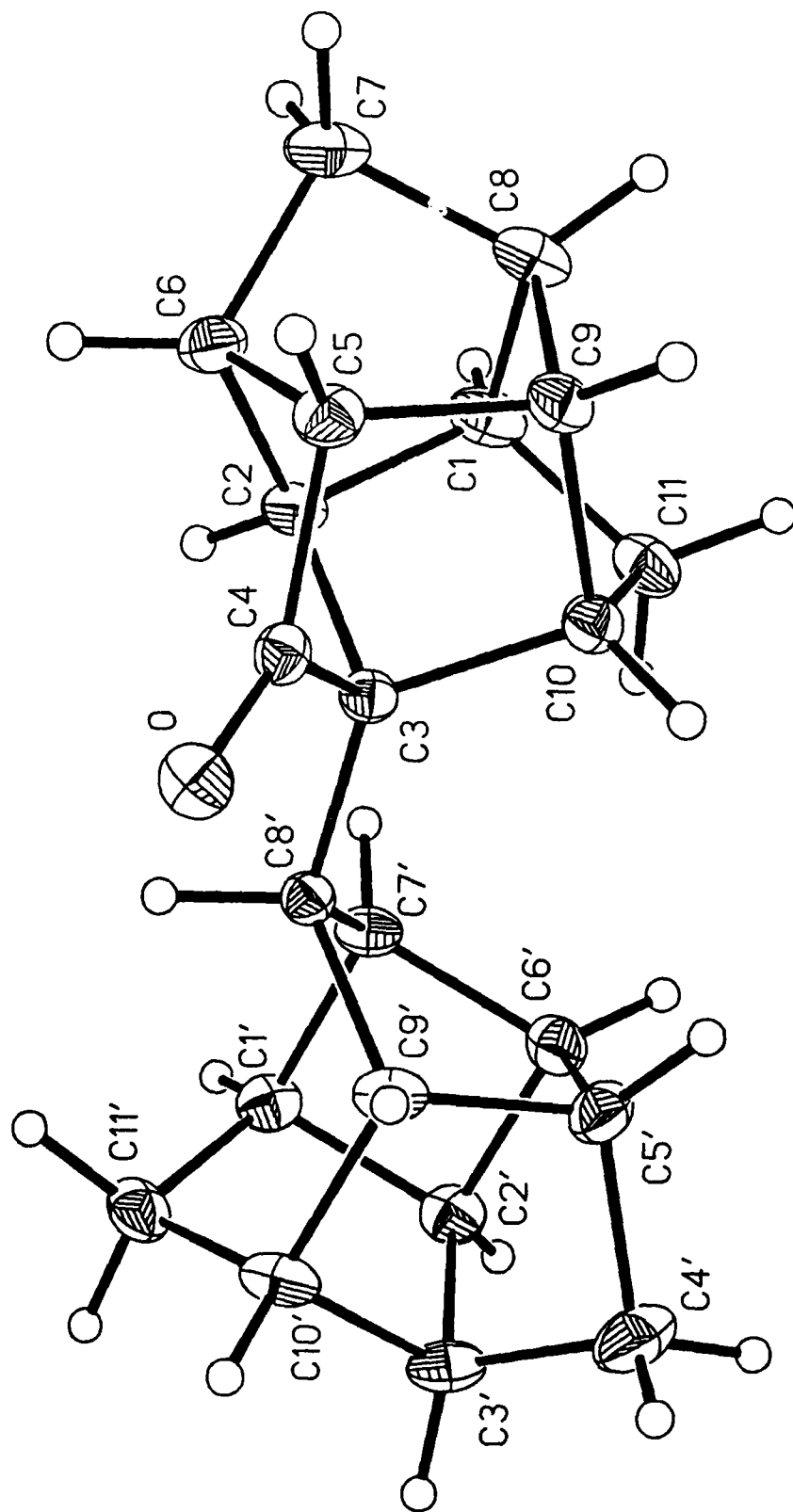


Figure 9. Structure drawing of 7a

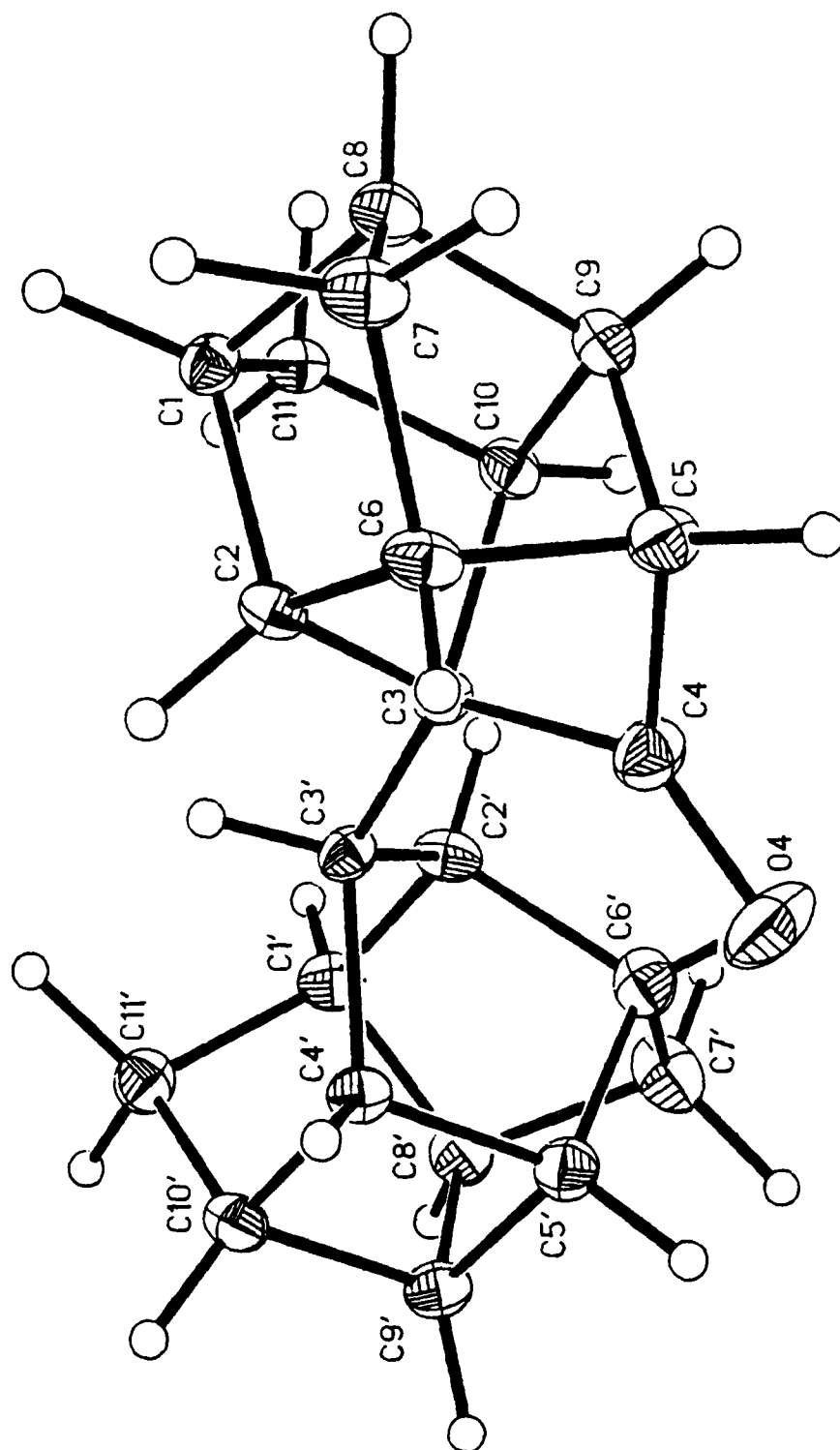
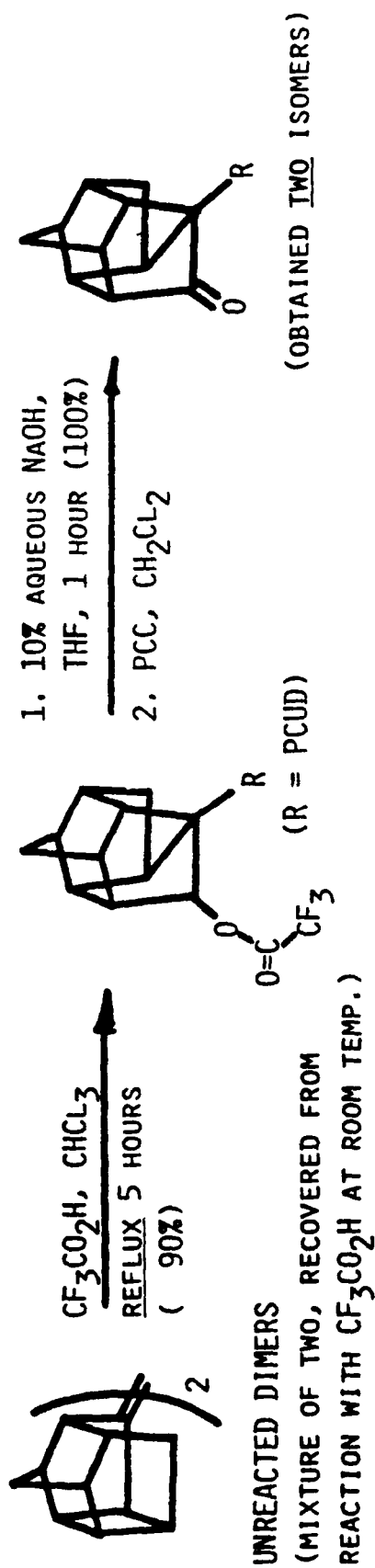


Figure 10. Structure drawing of 7b





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Figure 11. Further reaction of the "unreacted PCUD dimers" (see Figure 8) with refluxing trifluoroacetic acid

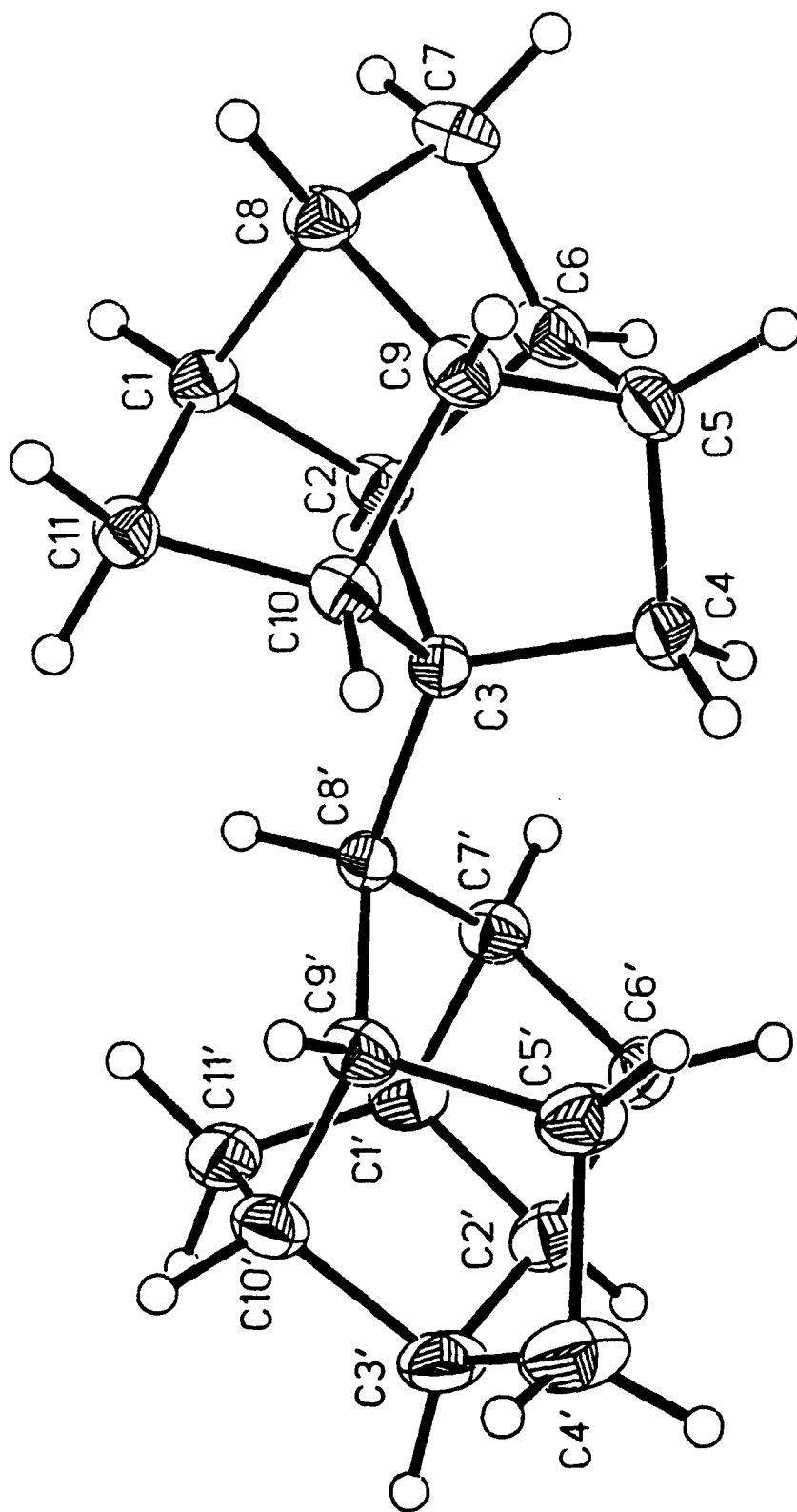


Figure 12. Structure drawing of 8a

DIMERS DERIVED FROM  $D_3$ -TRISHOMOCUBANONE

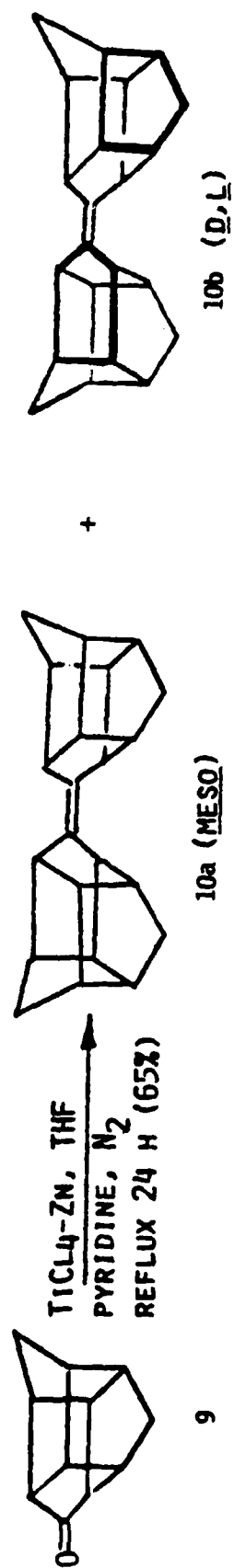
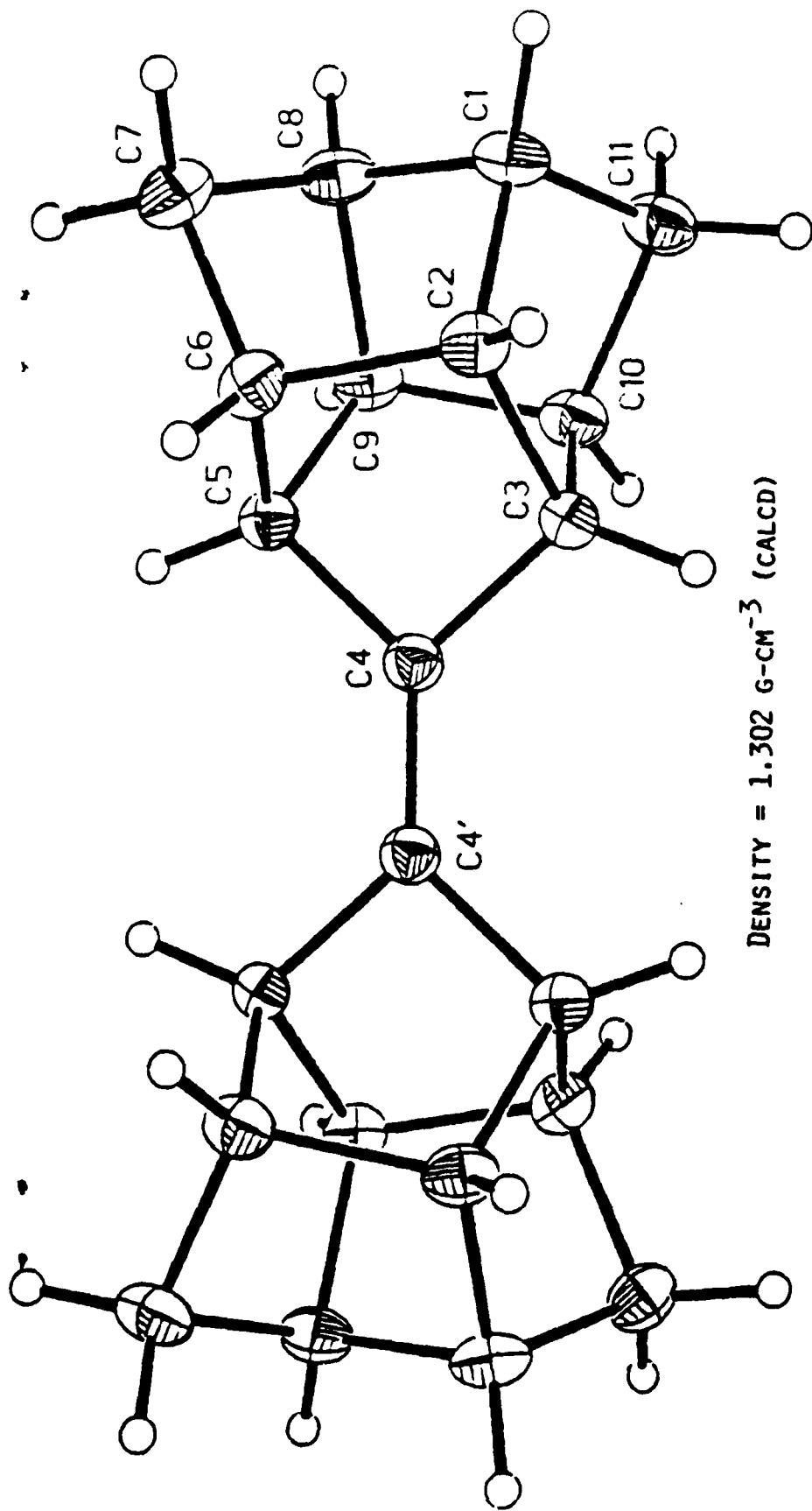
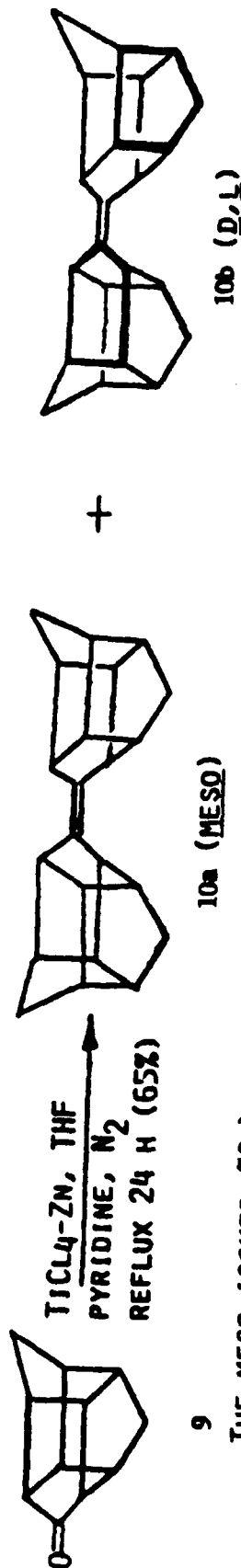


Figure 13. Synthesis of 10a and 10b



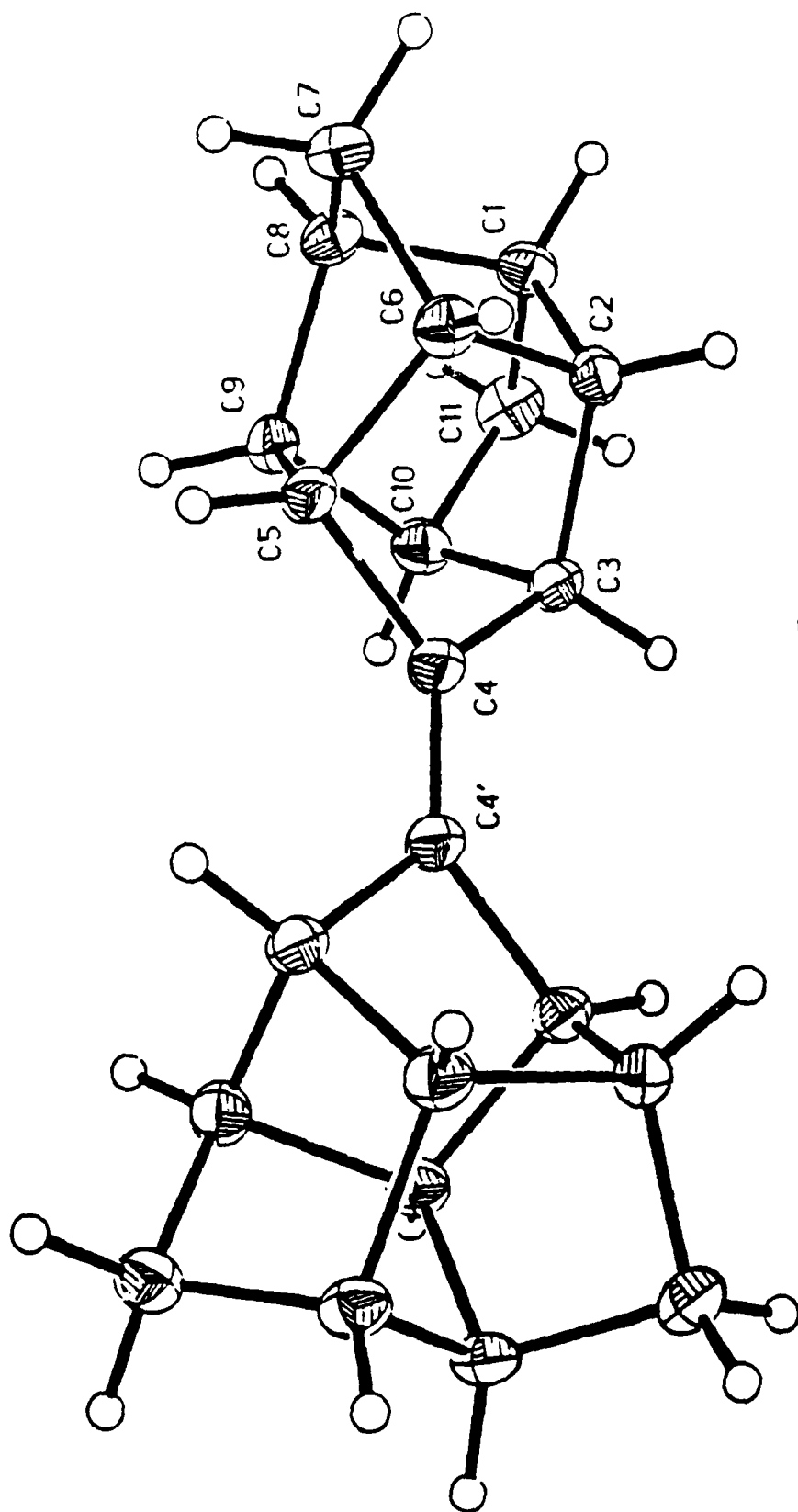
DENSITY = 1.302 G-CM<sup>-3</sup> (CALCD)



THE MESO ISOMER (10a) WAS ISOLATED VIA CAREFUL FRACTIONAL RECRYSTALLIZATION OF THE PRODUCT MIXTURE FROM LIGROIN. THE MATERIAL THEREBY OBTAINED DISPLAYED MP 246 °C.

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X-RAY CRYSTALLOGRAPHY: WILLIAM H. WATSON AND ANTE NAGL, DEPARTMENT OF CHEMISTRY,  
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Figure 14. Structure drawing of 10a



DENSITY = 1.269 G-CM<sup>-3</sup> (CALCD)

WE HAVE ALSO ISOLATED THE D,L DIMER, 10b, MP 186 °C (RECRYSTALLIZED FROM HEXANE-ETHER). THE D,L ISOMER CRYSTALLIZES IN SPACE GROUP P1̄ (TRICLINIC); IT IS SIGNIFICANTLY LESS DENSE THAN THE CORRESPONDING MESQ ISOMER (SPACE GROUP C2/c, MONOCLINIC, DENSITY = 1.302 G-CM<sup>-3</sup>).  
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X-RAY CRYSTALLOGRAPHY: WILLIAM H. WATSON AND ANTE NAGL, DEPARTMENT OF CHEMISTRY  
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Figure 15. Structure drawing of 10b